Rate-Controlled Constrained-Equilibrium (RCCE) Modeling of Propulsive Performance of Energetic Materials in a Hypersonic Nozzle

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Abstract

The rate-controlled constrained-equilibrium (RCCE) method for simplifying the kinetics of complex reacting system is reviewed. This method is based on the maximum entropy principle of thermodynamics and involves the assumption that evolution of a system can be described using few set of slowly changing constraints imposed by external and internal dynamics of the system. As a result, the number of differential and algebraic equations required to determine the constrained-equilibrium state of a system can be very much smaller than the number of species. The method has been applied to the oxidation of methane in a constant volume adiabatic chamber. The results of using 12 constraints (12 differential equations) are in perfect agreement with detailed chemistry using 29 species. The model, then, was applied to the expansion of combustion products of methane during the power stroke of an internal combustion engine. Results of using 8 constraints were in an excellent agreement with those of detailed chemistry. Reacting gas mixture through a nozzle was analyzed using detailed chemistry, and properties such as temperature and pressure as a function of location were determined. The combined analysis of flow through nozzle and rate-controlled constrained-equilibrium model has been developed and calculations are being made now.

1. Introduction

The development of models for describing the dynamic evolution of chemically reacting systems is a fundamental objective of chemical kinetics. The conventional approach to this problem involves first specifying the state and species variables to be included in the model, compiling a "full set" of rate-equations for these variables, and integrating this set of equations to obtain the time-dependent behavior of the system. Such models are frequently referred to as "Detailed Kinetic Model"s (DKMs).

The problem is that the detailed kinetics of C/H/O/N molecules can easily involve hundreds of chemical species and isomers, and thousands of possible reactions even for system containing only C_1 molecules. Clearly, the computational effort required to treat such systems is extremely large. The difficulties are compounded when considering reacting turbulent flows, where the complexity of turbulence is added to that of the chemistry.

As a result a great deal of effort has been devoted to developing methods for reducing the size of DMKs. Among the most prominent are: Quasi Steady State Approximation (QSSA) [1], Partial Equilibrium Approximation [2], Intrinsic Low Dimensional Manifolds (ILDM) [3], Computational Singular Perturbation (CSP) [4], Adaptive Chemistry [5], Directed Relation Graph (DRG) [6] and The ICE-PIC method [7].

An alternative approach, originally proposed by Keck and Gillespie [8] and later developed and applied by Keck and co-workers [9-11], and others [12-15] is the Rate-Controlled Constrained-Equilibrium (RCCE) method. This method is based on the maximum entropy principle of thermodynamics and involves the fundamental assumption that slow reactions in a complex reacting system impose constraints on its composition which control the rate at which it relaxes to chemical equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints.

An advantage of the RCCE method is that it does not require a large DKM as a starting point. Instead, one starts with a short list of constraints and rate-limiting reactions, to which more can be added to improve the accuracy to the desired level. If the only constraints are those imposed by slowly changing state variables, the RCCE method is equivalent to a local-chemical-equilibrium (LTE) calculation. If the number of constraints in an RCCE model is identical to the number of species in a DKM model, then the total number of equations, differential plus algebraic, to be solved will be identical and the results will be similar but not identical to those of the DKM model. The DKM will include only the specified species whereas the RCCE model will include implicitly all species which can be made from the elements in the system.

As with all thermodynamic systems, the number of constraints necessary to describe the dynamic state of the system within measurable accuracy can be very much smaller than the

number of species in the system. Therefore, fewer equations are required to describe the evolution of the system. A further advantage is that only rates of the slow constraint changing reactions are needed and these are the ones most likely to be known. Reactions which do not change any constraint are in equilibrium and need not be specified. It should be emphasized that the successful implementation of the RCCE method depends critically on the constraints employed and a knowledge of the rates of the constraint changing reactions is required. When rates are uncertain or unknown, the Principle of Bayesian Inference suggests that the best choice is to assume that the corresponding reactions are in constrained-equilibrium (CE).

The purpose of this project was to investigate the application of RCCE to nozzle flow analysis. During this period, evolution of a reacting system in a constant volume, initially far from equilibrium state, was modeled successfully using RCCE and results have been published in Combustion and Flame [16]. The next immediate step was to study kinetic effects in a rapidly expanding volume, containing a mixture initially at chemical equilibrium. The model considered was expansion of combustion products in a cylinder of an internal combustion engine. The change in the thermodynamic state due to expansion causes changes in chemical composition. The faster the expansion the lesser the time to adjust to the new thermodynamic state and the more pronounced the nonequilibrium effects. The chemical phenomena observed under such conditions are expected to be similar to those in a rapidly expanding nozzle flow. The results of volume expansion have been published in International Journal of Thermodynamics [17]. The research effort has been then followed by analyzing flow through nozzle. The governing equations using detailed kinetics were solved and results are presented. The combined analysis of flow through nozzle and rate-controlled constrained-equilibrium model has been developed, shown in section 7.2, and calculations are being made now.

2. Rate-Controlled Constrained-Equilibrium (RCCE) Method

A detailed description of the Rate-Controlled Constrained-Equilibrium (RCCE) method is given in reference [18]. A concise summary of the working equations for chemically reacting gas mixtures is given below.

It is assumed that energy exchange reactions are sufficiently fast to equilibrate the translational, rotational, vibrational, and electronic degrees of the system subject to constraints on the volume, V, and the total energy , E, of the system. Under these conditions, the energy can be written

$$E = \underline{E}^T(T)\underline{N} \tag{1}$$

where $\underline{E}^T(T)$ is the transpose of the species molar energy vector and T is the temperature and $\underline{N}$ is the vector of species mole numbers. It is further assumed that the perfect gas model applies

and the species constraints, $\underline{C}$, can be expressed as a linear combination of the species mole numbers in the form

$$\underline{C} = \underline{\underline{A}}\underline{N} \tag{2}$$

where, $\underline{\underline{A}}$ is the $n_c \times n_{sp}$ constraint matrix, n_c is the number of constraints, n_{sp} is the number of species and $\underline{C}$ and $\underline{N}$ are column vectors of length n_c and n_{sp}. Maximizing the Entropy, *S(E, V, C)*, subject to the constraints (2) using the method of undetermined Lagrange multipliers, [18], we obtain the constrained-equilibrium composition of the system

$$\underline{N}^c = (M/p)\exp(-\underline{\mu}^0 - \underline{\mu}^c) \tag{3}$$

where *M* is the total mole number, *p=MRT/V* is the pressure, $\underline{\mu}^0 = (\underline{h}^0 - T\underline{s}^0)/RT$ is the dimensionless standard Gibbs free energy for n_{sp} species, and

$$\underline{\mu}^c = -\underline{\underline{A}}^T \underline{\gamma} \tag{4}$$

is the dimensionless constrained-equilibrium Gibbs free energy of the species. In Eq. (4), $\underline{\underline{A}}^T$ is the transpose of the constraint matrix, and $\underline{\gamma}$ is the vector of dimensionless constraint potentials (Lagrange multipliers) conjugate to the constraint vector, $\underline{C}$.

Given the values of the constraints, $\underline{C}$, and energy, *E*, of the system, substitution of Eq. (3) into Eqs. (1) and (2) gives a set of n_c+1 transcendental equations which can be solved for the temperature, $T(E,V,\underline{C},\underline{\mu}^\circ)$, and the constraint potentials, $\underline{\gamma}(E,V,\underline{C},\underline{\mu}^\circ)$, using generalized equilibrium codes such as GNASA [19] or GSTANJAN [19]. Finally substituting Eq. (4) into Eq. (3) gives the constrained-equilibrium composition of the system, $\underline{N}^c(E,V,\underline{C},\underline{\gamma})$.

2.1. Rate-equations for the constraints

It is assumed that changes in the chemical composition of the system are the results of chemical reactions of the type

$$\underline{\underline{v}}^- \underline{X} \leftrightarrow \underline{\underline{v}}^+ \underline{X} \tag{5}$$

where $\underline{X}$ is the species vector, $\underline{\underline{v}}^-$ and $\underline{\underline{v}}^+$ are $n_r \times n_{sp}$ matrices of stoichiometric coefficients of reactants and products respectively, and n_r is the number of reactions. The corresponding rate-equations for the species can be written

$$\underline{\dot{N}} = V\underline{\underline{v}}\underline{r} \tag{6}$$

where $\underline{\underline{v}} = \underline{\underline{v}}^+ - \underline{\underline{v}}^-$, $\underline{r} = \underline{r}^+ - \underline{r}^-$, and $\underline{r}^+$ and $\underline{r}^-$ are the forward and reverse reaction rate column vectors of length n_r

Differentiating Eqs. (1) and (2) with respect to time and using Eq. (6), we obtain equations for the energy

$$\dot{E}=\dot{T}\underline{C}_v^T\underline{N}+\underline{E}^T\underline{\dot{N}} \tag{7}$$

and constraints

$$\underline{\dot{C}}=\underline{\underline{A}}\underline{\dot{N}}=V\underline{\underline{B}}\underline{r} \tag{8}$$

where

$$\underline{\underline{B}}=\underline{\underline{A}}\underline{\underline{v}} \tag{9}$$

is an $n_c \times n_r$ matrix giving the change of constraints due to the n_r elementary chemical reactions among species and $\underline{C}_v \equiv \partial \underline{E}/\partial T$ is the molar specific heat vector at constant volume. It follows from Eq. (9) that a reaction k for which all B_{ik} are zero will be in constrained-equilibrium and that a constraint i for which all B_{ik} are zero will be conserved. The latter is assumed to be the case for the elements.

Given equations for the state-variables, $V(t)$ and $E(t)$, and initial values for the species, $\underline{N}(0)$, Eqs. (7) and (8) can be integrated in stepwise fashion to obtain the temperature, $T(t)$ and species constraints, $\underline{C}(t)$. At each time step, a generalized equilibrium code, such as GNASA or GSTANJAN previously cited, must be used to determine the temperature, $T(E,V,\underline{C},\underline{\mu}^\circ)$, and constrained-equilibrium composition, $\underline{N}^c(E,V,\underline{C},\underline{\mu}^\circ)$. These, in turn, can be used to evaluate the reaction rates $\underline{r}(T,V,\underline{\mu}^\circ,\underline{v},\underline{N}^c)$ required for the next step. Note that only the rates of reactions which change constraints, i.e. those for which $B_{ik}\neq0$, are required for RCCE calculations. All other reactions are in constrained-equilibrium and need not be specified.

3. Rate equations for the constraint potentials

Although direct integration of the rate-equations for the constraints is relative straight forward and simple to implement, it has proved to be relatively inefficient and time consuming due to the slowness of the constrained-equilibrium codes currently available [19]. An alternative method, first proposed by Keck [18] and implemented in later works [19,20] with colleagues, is the direct integration of the rate-equations for the constraint-potentials. This method has also recently been investigated by Tang and Pope [5] and Jones and Rigopoulos [6].

Differentiating Eq. (3) with respect to time and substituting the result into Eq. (7) and (8) yields the n_c+1 implicit equations for the energy,

$$\underline{\underline{D}}_\Gamma \dot{\underline{\chi}} - \underline{D}_V \frac{\dot{V}}{V} - \underline{D}_T \frac{\dot{T}}{T} + \dot{\underline{E}} = 0 \tag{10}$$

where

$$D_{\Gamma i} = \sum_j a_{ij} E_j N_j^c \tag{10a}$$

$$D_V = \sum_j E_j N_j^c \tag{10b}$$

$$D_T = \sum_j (C_{vj} T + E_j^2 / RT) N_j^c \tag{10c}$$

and the constraint-potentials,

$$\underline{\underline{C}}_\Gamma \dot{\underline{\chi}} - \underline{C}_V \frac{\dot{V}}{V} - \underline{C}_T \frac{\dot{T}}{T} + \underline{\underline{Br}} = 0 \tag{11}$$

where

$$C_{\Gamma ik} = \sum_j a_{ij} a_{kj} N_j^c \tag{11a}$$

$$C_{Vi} = \sum_j a_{ij} N_j^c \tag{11b}$$

$$C_{Ti} = \sum_j a_{ij} E_j N_j^c / RT \tag{11c}$$

In this case, given equations for the state variables, $V(t)$ and $E(t)$, and the initial temperature, $T(0)$, and constraint-potentials, $\gamma(0)$, Eqs. (10) and (11) can be integrated using implicit ODE integration routines such as DASSL [7] to obtain the temperature, $T(t)$, and constraint potentials, $\chi(t)$. The constrained-equilibrium composition, $\underline{N}^c(E, V, \text{t})$, of the system can then be determined using Eq. (3). The number of unknowns is reduced from the $n_{sp}+1$ in a DKM calculation to n_c+1 in the RCCE calculation. As previously noted, only the rate constants for those reactions which change constraints, i.e. $B_{ik} \neq 0$, are needed. Note that, once the constraint-potentials have been determined, the constrained-equilibrium concentration of any species for which the standard Gibbs free energy is known can be calculated whether or not it is explicitly included in the species list. It also follows that all species are implicitly included in the RCCE rate-equations.

4. Selection of constraints

The careful selection of constraints is the key to the success of the RCCE method. Among the general requirements for the constraints are that they must a) be linearly independent combinations of the species mole numbers, b) hold the system in the specified initial state, c) prevent global reactions in which reactants or intermediates go directly to products and, d)

determine the energy and entropy of the system within experimental accuracy. In addition, they should reflect whatever information is available about rate-limiting reactions which control the evolution of the system on the time scale of interest.

In the present work, the focus is on applications of the RCCE method to chemically reacting gas phase mixtures. In the temperature and pressure range of interest, the rates of nuclear and ionization reactions are negligible compared to those for chemical reactions and the fixed constraints are the *neutral elements* of hydrogen, carbon, oxygen, nitrogen,..., designated by EH, EC, EO, EN,…

Under these conditions, the slowest reactions controlling the chemical composition are three-body dissociation/recombination reactions and reactions which make and break valence bonds. Such reactions are slow in the endothermic direction because of the high activation energies required, and in the exothermic direction because of small three-body collision rates and small radical concentrations. They impose slowly varying time-dependent constraints on the number of *moles*, M, of gas and the *free valence,* FV, of the system respectively. A finite value of FV is a necessary condition for chain branching chemical reactions to proceed.

A third important time-dependent constraint, imposed by slow OO bond-breaking reactions, is the *free-oxygen*, FO, defined as any oxygen atom not directly bound to another oxygen atom. An increase in FO is a necessary condition for the formation of the major reaction products of hydrocarbon oxidation, H_2O, CO_2 and CO.

Two additional time-dependent constraints which slightly improve the agreement between RCCE and DKM calculations under some conditions are: $OHO \equiv OH+O$ and $DCO \equiv$ $HCO+CO$. The OHO constraint is a consequence of the relatively slow constraint changing reaction $RH+OH \leftrightarrow H_2O+R$ coupled with the fast reaction $RH+O=OH+R$ which equilibrates OH and O. The DCO constraint is a consequence of the slow spin-forbidden reaction $CO+HO_2 \leftrightarrow$ CO_2+OH coupled with the fast reaction $HCO+O_2=CO+HO_2$ which equilibrates HCO and CO.

For systems involving the elements C, H and O the 8 constraints EH, EO, EC, M, FV, FO, OHO, and DCO are independent of the initial reactants and may, therefore, be considered "universal" constraints. Along with the equilibrium reactions,

$$H_2+O=OH+H \tag{CE1}$$
$$H_2+HOO=H_2O_2+H \tag{CE2}$$
$$HCO+O_2=CO+HO_2 \tag{CE3}$$

they are sufficient to determine the constrained-equilibrium mole fractions of the 11 major hydrocarbon combustion products H, O, OH, HO_2, H_2, O_2, H_2O, H_2O_2, HCO, CO and CO_2 under both high and low temperature conditions.

In the present investigation of C_1-hydrocarbon oxidation, 4 additional fuel-dependent constraints have been used. The first is a constraint on the *fuel*, FU, imposed by slow hydrogen – abstraction reactions of the type $FU+O_2 \leftrightarrow FR+HO_2$ and even slower dissociation/recombination of the type $AB+M \leftrightarrow A+B+M$. This constraint is necessary to hold the system in its initial state.

The second is a constraint on *fuel radicals*, FR, which is necessary to prevent the equilibration of forbidden exothermic global reactions such as $CH_3+2O_2+2H_2O=CO_2+2H_2O_2+H_2+H$ which would otherwise convert fuel radicals directly to major products. The third is a constraint on *alkylperoxides*, $APO \equiv CH_3OOH+CH_3OO+CH_2OOH$, imposed by slow reactions which convert APO to hydroperoxides coupled with fast reactions which equilibrate the species comprising APO, and the fourth is a constraint on *alcohol plus formaldehyde*, $ALCD \equiv CH_3OH+CH_3O+CH_2OH+CH_2O$ imposed by relatively slow reactions which generate/remove ALCD coupled with fast reactions which equilibrate the species comprising ALCD.

5. CH$_4$ Results for 133 Reaction Set

Time-dependent temperature profiles of stoichiometric mixtures of methane and oxygen at initial temperatures of 900K and 1500K and different initial pressures are shown in Fig. 1. The 12 constraints used are listed in table 1. Under this set of constraints, only 102 of the reactions in the full set of 133 reactions change constraints and are therefore required. The remaining 31 are in constrained-equilibrium and are not needed in RCCE calculations.
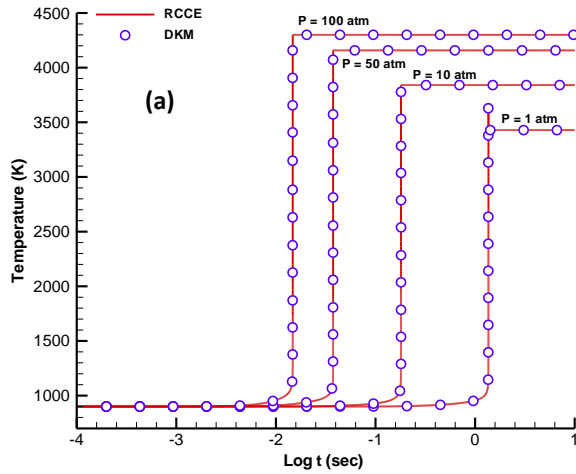

Figure 1: Comparison of RCCE and DKM temperature vs time profiles for a stoichiometric mixture of CH_4/O_2 at different initial pressures and initial temperatures of 900 K and 1500 K. (Time in sec)
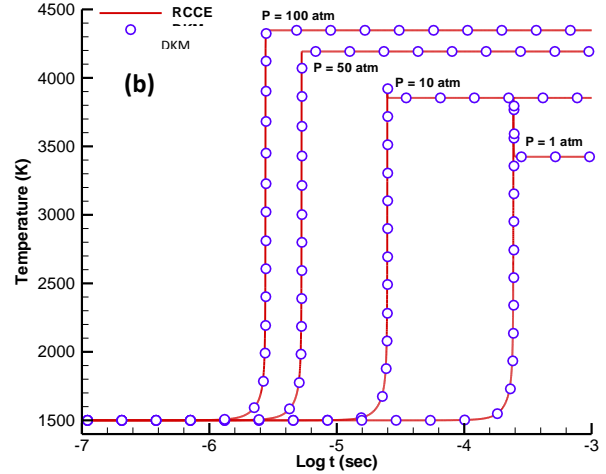
Figure 2: Comparison of RCCE and DKM temperature vs time profiles for CH_4/O_2 mixtures with different equivalence ratios at initial temperatures and pressures of 900 K and 100 atm (a) and 1500 K and 1 atm (b). (time in sec)

It can be seen that the agreement with DKM calculations is excellent over the entire range of pressure and temperature covered. Note that the temperature overshoot at low pressures due to

slow three-body recombination and dissociation reactions is well reproduced by the constraint M on the total moles.

Additional results are shown on log-log plots in Fig. 2 for the initial conditions 900 K and 100 atm, where the dominant radicals are $HO_2 \approx CH_3$ at early times and CH3OO at late times and in Fig. 3 for the initial conditions 1500 K and 1atm, where the dominant radicals are $HO_2 \approx CH_3OO$ at all times. As can be seen in Figs 2a and 3a, the temperature first decreases due to the fact that the initiation reactions are all endothermic then later increases as exothermic reactions become important. The agreement between RCCE and DKM calculations, especially with regard to the time at which the temperature difference becomes positive, is excellent.

The fixed elemental constraints and the most important time-dependent constraints M, FV, FO, FU and FR are shown in Figs 2d and 3d and the mole fractions of the major species are shown in Figs 2e-h and 3e-h. It can be seen that overall agreement is very good. A detailed presentation of this research has been published in Combustion and Flame [16].

6. Power Stroke of and Internal Combustion Engine

The physical model considered for this part of the research is shown in figure 4. It is assumed that the power stroke begins with the combustion products at a complete chemical equilibrium state and that expansion occurs so rapidly that heat conduction does not occur through the piston wall. It is further assumed that the gas composition is homogeneous at any time during expansion. Volume is assumed to be a prescribed function of time.
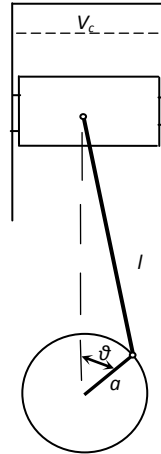

Figure 4: Schematic of the physical model

Figure 3: Comparison of various RCCE and DKM time profiles for stoichiometric CH$_4$/O$_2$ mixtures at initial temperature and pressure of 900 K and 100 atm. (time in sec)

Figure 4: Comparison of various RCCE and DKM time profiles for stoichiometric CH_4/O_2 mixtures at initial temperature and pressure of 1500 K and 1 atm. (time in sec)

	Constraint	Definition of the Constraint
1	EC	Elemental carbon
2	EO	Elemental oxygen
3	EH	Elemental hydrogen
4	M	Total number of moles
5	FV	Moles of free valance (any unpaired valence electron)
6	FO	Moles of free oxygen (any oxygen not directly attached to another oxygen)
7	OHO	Moles of water radicals (O+OH)
8	DCO	Moles of HCO+CO
9	FU	Moles of fuel molecules
10	FR	Moles of fuel radicals
11	APO	Moles of AlkyPerOxydes ($CH_3OO+CH_3OOH+CH_2OOH$)
12	ALCD	Moles of Alcohols+Aldehydes ($CH_3O+CH_3OH+CH_2OH+CH_2O$)

The general formulation remains the same. However, the time rate of change of volume in equations (10) and (11) is no longer zero in this case. The constraints used in this study include EH, EO, EC, EN (elemental nitrogen), M, FV, FO and DCO from table 1.

According to the Le Châtelier principle, when a highly dissociated mixture undergoes an interaction with the environment which lowers the gas temperature and density, the internal dynamics shift in the exothermic direction to minimize the cooling effect of interaction. As a result, three body recombination reactions become an important part of the energy restoration process. The total number of particles in the system does not change unless one such reaction occurs. Figures 5 and 6 represent comparison of the detailed kinetics against RCCE when constraints are added on at a time. RCCE is able to handle cases as different as frozen equilibrium, fully rate controlled and local thermodynamic equilibrium (L.T.E) with the same ease. The result of this part of the research has been published in International Journal of Thermodynamics [17].

7. Governing Equations for an Expanding Nozzle Flow

7.1. Detailed Kinetic Formulation

Assuming an inviscid, adiabatic and steady flow, it is easy to show that the enthalpy is conserved and the governing equations take the following form:

Overall Continuity
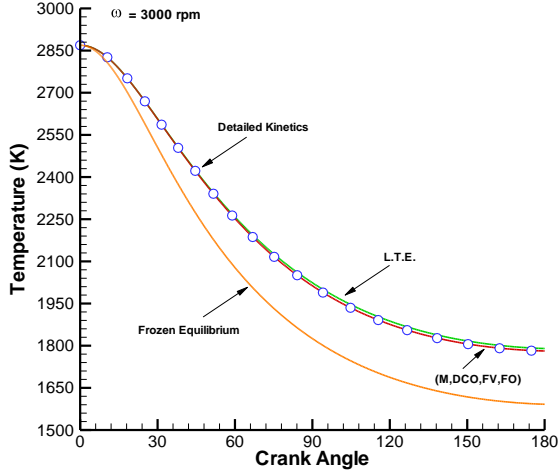
$$\rho u A(x) = \dot{m} = cte \tag{12}$$

Figure 5: Temperature profiles under different sets of constraints compared with the predictions of detailed kinetics at an engine speed of 3000 rpm
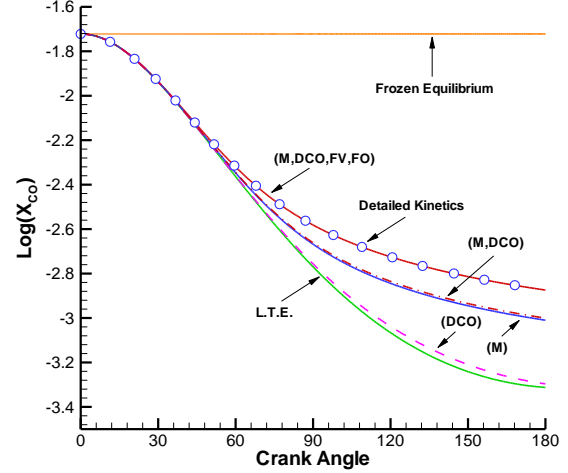

Figure 6: Constraint-dependence of CO profiles compared with the predictions of detailed kinetics at an engine speed of 3000 rpm

Momentum Equation

$$u\frac{du}{dx}+\frac{dp}{dx}=0 \tag{13}$$

Species Mass Balance

$$\rho u\frac{dY_i}{dx}-\dot{\omega}_i M_i =0 \tag{14}$$

Energy Equation

$$\left(\sum_{i=1}^{N_{sp}}C_{p,i}Y_i\right)\frac{dT}{dx}+\sum_{i=1}^{N_{sp}}h_i\frac{dY_i}{dx}+u\frac{du}{dx}=0 \tag{15}$$

Equation of State

$$p=\frac{\rho}{\overline{M}}R_u T \tag{16}$$

where ρ, u, $A(x)$, p and T are density, convective velocity, nozzle area, pressure and temperature respectively. Also, Y_i, h_i, $C_{p,i}$ and N_{sp} represent, respectively, the mass fraction, total enthalpy (formation + sensible), heat capacity at constant pressure of species i and number of species. $\dot{\omega}_i$ is the net molar rate of consumption of species i and M_i is its molecular mass. The mixture molecular mass $\overline{M}$ is also determined as follows:

$$\frac{1}{M} = \sum_{i=1}^{N_{sp}} \frac{Y_i}{M_i} \qquad (17)$$

Note that the energy equation (15) can be further simplified by replacing for $\dfrac{dY_i}{dx}$ from equation (14) as:

$$\rho u \left(\sum_{i=1}^{N_{sp}} C_{p,i} Y_i \right) \frac{dT}{dx} + \sum_{i=1}^{N_{sp}} h_i \dot{\omega}_i M_i + \rho u^2 \frac{du}{dx} = 0 \qquad (18)$$

The initial condition is taken to be a C/H/O system at chemical equilibrium. Such initial condition can be easily obtained using STANJAN program. The flow is subsonic up to the throat section. Therefore, it is a reasonable to assume that the mixture is in chemical equilibrium. Departures from equilibrium happen due to expansion in the divergent section as a result of insufficient residence time. In the current study we consider the expansion downstream of the throat section and specify an equilibrium mixture at this section. Equations (13) through (18) are then solved under an area profile presented in section 7.3. The initial temperature is 2000 K and the initial pressure is 20 atm and the initial velocity is 900 m/sec. Figs 7 and 8 show the temperature and pressure profiles within the divergent section of the nozzle. The exit-to-throat area ratio is assumed 10, the nozzle length is assumed 2m, and the throat area 1m².
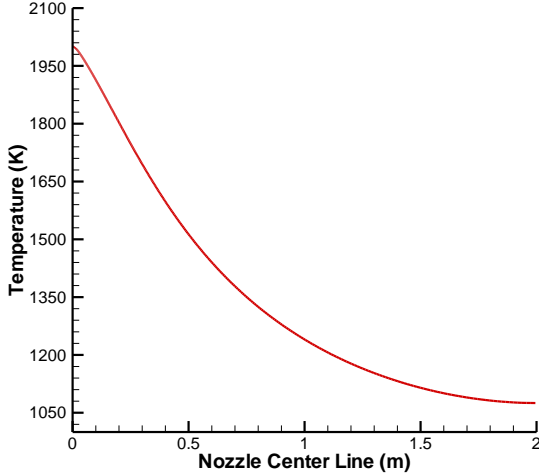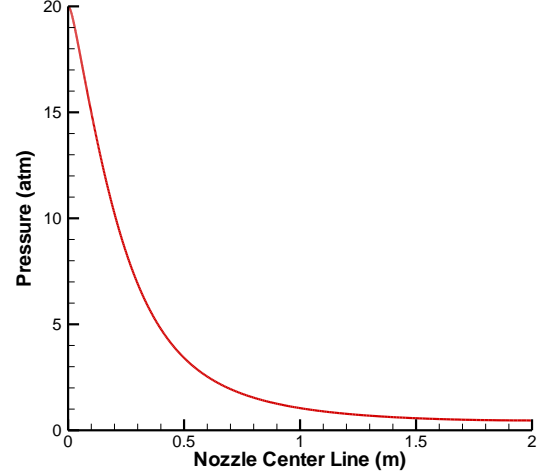

Figure7:Temperature profiles along the axis of nozzle.

Figure 8: Pressure profiles along the axis of nozzle.

7.2. RCCE Formulation

Equations (12) and (13) remain invariant under RCCE transformations. In what follows the RCCE form of the species continuity, the energy equation and the equation of state are derived.

Species Mass Balance

Multiplying equation (14) through by $A(x)$ and then using the continuity equation, and also using the relation $\rho = [N_i]M_i$, one can easily obtain the following form for the species equation:

$$[N_i]\frac{du}{dx} + u\frac{d[N_i]}{dx} + u[N_i]\left(\frac{1}{A}\frac{dA}{dx}\right) = \dot{\omega}_i \tag{19}$$

The RCCE distribution of concentrations is also given as [1]:

$$[N_i] = Q_i \exp\left(-\sum_{j=1}^{N_c} a_{ij}\gamma_j\right) \tag{20}$$

Differentiating equation (20) with respect to x yields:

$$\begin{aligned}
\frac{d[N_i]}{dx} &= [N_i]\left(\frac{1}{Q_i}\frac{dQ_i}{dx}\right) - [N_i]\sum_{j=1}^{N_c} a_{ij}\frac{d\gamma_j}{dx}\\
&= \left(\frac{E_i[N_i]}{R_u T^2}\right)\frac{dT}{dx} - [N_i]\sum_{j=1}^{N_c} a_{ij}\frac{d\gamma_j}{dx}
\end{aligned} \tag{21}$$

Now, multiplying equation (19) by a_{ik}, summing over species index i and then using the equation (21), we will have:

$$u\sum_{j=1}^{N_c} f_{jk}\frac{d\gamma_j}{dx} - ul_k\left(\frac{1}{T}\frac{dT}{dx}\right) - C_k\frac{du}{dx} - uC_k\left(\frac{1}{A}\frac{dA}{dx}\right) + \sum a_{ik}\dot{\omega}_i = 0 \tag{22}$$

where

$$f_{jk} = \sum_{i=1}^{N_{sp}} a_{ij}a_{ik}[N_i]$$

$$l_k = \sum_{i=1}^{N_{sp}} a_{ik}[N_i]\frac{E_i}{R_u T}$$

$$C_k = \sum_{i=1}^{N_{sp}} a_{ik}[N_i]$$

Energy Equation:

The energy equation in this case is equivalent with the conservation of stagnation enthalpy, that is:

$$H_\circ = h + \frac{1}{2}u^2 = cte \tag{23}$$

where

$$h = \sum_{i=1}^{N_{sp}} Y_i h_i = \frac{1}{\rho} \sum_{i=1}^{N_{sp}} \rho_i h_i = \frac{1}{\rho} \sum_{i=1}^{N_{sp}} [N_i] M_i h_i \tag{24}$$

The energy equation can then be written in the following form:

$$\rho H_\circ = \sum_{i=1}^{N_{sp}} Y_i h_i = \sum_{i=1}^{N_{sp}} [N_i] M_i h_i + \frac{1}{2} \rho u^2 \tag{25}$$

Differentiating equation (25) with respect to x and using equation (2) results in the following form for energy equation:

$$-\sum_{i=1}^{N_{sp}} E_{yj} \frac{d\gamma_j}{dx} + E_T \frac{dT}{dx} + \rho u \frac{du}{dx} + (\frac{1}{2}u^2 - H_\circ)\frac{d\rho}{dx} = 0 \tag{25}$$

where

$$E_{yj} = \sum_{i=1}^{N_{sp}} [N_i] M_i h_i a_{ij}$$

$$E_T = \sum_{i=1}^{N_{sp}} [N_i] M_i \left(\frac{h_i E_i}{R_u T^2} + c_{pi} \right)$$

and $H_\circ$ is the stagnation enthalpy per unit mass at nozzle throat, which is constant everywhere.

Equation of State:

Re-writing equation (16) using the relation $\rho = [N_i] M_i$ in equation (17) results in the following familiar form for the equation of state:

$$p = \sum_{i=1}^{N_{sp}} [N_i] R_u T \tag{26}$$

Differentiating equation (26) with respect to x and then using equation (21) yields:

$$R_u T \sum_{i=1}^{N_{sp}} C_j \frac{d\gamma_j}{dx} + S \frac{dT}{dx} - \frac{dp}{dx} = 0 \tag{27}$$

where

$$S = \sum_{i=1}^{N_{sp}} [N_i]_i \left(\frac{E_i}{T} - R_u \right)$$

$$C_j = \sum_{i=1}^{N_{sp}} a_{ij} [N_i]$$

7.3   Nozzle Area Profile

Currently, the following profile has been used:

$$A(x) = ax^3 + bx^2 + cx + d \qquad (28)$$

The unknown coefficients a, b, c, d are determined such that the following geometrical constraints are satisfied:

$$A|_{x=0} = A_{th},$$

$$A|_{x=L} = A_{end},$$

$$\frac{dA}{dx}|_{x=0} = 0,$$

$$\frac{dA}{dx}|_{x=L} = 0 \qquad (29)$$

The nozzle geometry, under these boundary conditions, becomes:

$$\frac{A(x)}{A_{th}} = -2(A_r - 1)\left(\frac{x}{L}\right)^3 + 3(A_r - 1)\left(\frac{x}{L}\right)^2 + 1 \qquad (30)$$

Where

$$A_r = \frac{A_{end}}{A_{th}}$$

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